

2-ARYL DERIVATIVES OF CONDENSED FIVE-MEMBERED N-HETEROCYCLIC COMPOUNDS. III.*

IR ABSORPTION SPECTRA OF *ortho*- AND *para*-SUBSTITUTED PHENOLS AND NAPHTHOLS

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The wavenumbers of $\tilde{\nu}_{(\text{OH})}$ stretching bands in *ortho*- and *para*-substituted phenols were measured in chloroform solution. A linear correlation between $\tilde{\nu}_{(\text{OH})}$ and Hammett's $\bar{\sigma}_p$ constants has been found. The wavenumbers of the OH stretchings in *ortho*-substituted phenols and their deuterated analogues were measured in tetrachloromethane. A strong intramolecular hydrogen bond was found in all the *ortho*-substituted 2-[4,5]-aryleneazolyphenols. Both the medium effect and the effect of the *ortho*-substituent structure upon the strength of the intramolecular hydrogen bond are discussed.

It is generally known that an intramolecular hydrogen bond is manifested in the infrared spectra by a shift of the wavenumbers of the hydroxyl group stretching vibrations towards the lower values. Sharp bands shifted to the region of 3570–3450 cm^{-1} showing small intensity changes or broad bands in the region of 3200–2500 cm^{-1} having a markedly lowered intensity are observed depending on the kind of the intramolecular hydrogen bond¹. Sharp bands appear in the IR spectra of simple bridged molecules (e.g. *ortho*-halogenated phenols), in whose molecules the intramolecular hydrogen bond is relatively weak. Broad bands of diminished intensity appear in the spectra of the compounds having the conjugated chelation that favors a strong intramolecular hydrogen bonding². The term "conjugated chelation" was introduced by Rasmussen and coworkers³ and defined as the molecule ability to form the resonance structures in the system of conjugated bonds. This theory was further extended by Shigorin⁴, who first used the term "quasiaromatic six-membered ring". The conjugation through an intramolecular hydrogen bond was also considered by Grinter⁵. Generally it can be stated that the intramolecular hydrogen bond of the type $\text{O}\cdots\text{H}-\text{O}$ is better understood than the bond of the type $\text{N}\cdots\text{H}-\text{O}$. The largest attention had been paid to the *ortho*-hydroxyphenones^{6–11}. The bond of the type $\text{N}\cdots\text{H}-\text{O}$ was most often studied in *ortho*-hydroxybenzimidazoles^{12,13}. A strong intramolecular hydrogen bond was noted by several authors in 2-(2-benzimidazolyl)phenol^{14,15}.

In our previous works we have examined the effect of the intramolecular hydrogen bonding upon the dissociation constants¹⁶ and the UV absorption spectra¹⁷ of the *ortho*-substituted phenols and naphthols having a nitrogen-containing heterocyclic substituent. In the presented work, we measured the wavenumbers of the free hydro-

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yl group stretching vibrations in the *para*-substituted phenols *I–XV* and in the 4-substituted 1-naphthol *XVI* and the wavenumbers of the bound hydroxyl group stretching vibrations in the *ortho*-substituted phenols *XVII–XXVIII* and in the 1-substituted 2-naphthol *XXIX* (Tables I and II). The accurate determination of the bound hydroxyl group frequencies was based on the deuteration of the studied compounds and on the assumed constant $\tilde{\nu}_{(\text{OH})}/\tilde{\nu}_{(\text{OD})}$ ratio. The relative strength of the intramolecular hydrogen bond in *ortho*-substituted phenols and naphthols was estimated from the values of $\tilde{\nu}_{(\text{OH})}$ and $\tilde{\nu}_{(\text{OD})}$, respectively.

EXPERIMENTAL

The materials used were described earlier^{16,17}. Compounds *XXIV* and *XXVI* were commercial chemicals of p.a. quality. IR absorption spectra were measured on a SP-100 G instrument (Unicam, England). Chloroform (p.a.) was purified by rectification on a multi-plate column. Tetrachloromethane of spectral grade was used. *ortho*-Substituted phenols were measured in CCl_4 .

TABLE I

Wavenumbers of Bands due to the O—H Stretching Vibrations and Hammett's σ_p Constants of Some *para*-Substituted Phenols in Chloroform

No	Substituent	$\tilde{\nu}_{(\text{OH})}$, cm^{-1}	σ_p^b
<i>I</i>	methyl	3 602	-0.170 ^c
<i>II</i>	hydrogen	3 600	0.000 ^c
<i>III</i>	chlorine	3 596	0.226 ^c
<i>IV</i>	2-indolyl	3 596	0.389
<i>V</i>	2-benzimidazolyl	2 470 ^{a,d}	0.480
<i>VI</i>	2-naphto[1,2- <i>d</i>]triazolyl	3 592	0.487
<i>VII</i>	2-indazolyl	3 591	0.487
<i>VIII</i>	N-methyl-2-benzimidazolyl	2 581 ^{a,e}	0.578
<i>IX</i>	2-benzthiazolyl	3 590	0.652
<i>X</i>	2-benzoxazolyl	3 590	0.684
<i>XI</i>	benzoyl	3 587	0.821
<i>XII</i>	acetyl	3 585	0.874 ^c
<i>XIII</i>	2-benzotriazolyl	3 248 ^{a,e}	1.024
<i>XIV</i>	formyl	3 580	1.126 ^c
<i>XV</i>	nitro	3 577.5	1.270 ^c
<i>XVI</i>	4-(2-benzotriazolyl)-1-naphthol ^f	3 590	—

^a Too low solubility. Measured in KCl pellets (1 mg of compound/0.4 g KCl). ^b Taken from the ref.¹⁶ ^c Taken from the ref.²⁷ ^d Broad band. Simultaneously are present: a sharp of the free O—H stretching at $3\,601\text{ cm}^{-1}$ and a broad band of $\tilde{\nu}_{(\text{NH})}$ at $3\,242\text{ cm}^{-1}$. ^e Broad bands due to an intermolecularly bonded OH group ^f This compound has not the general structure given above.

(concentration $1.8 \cdot 10^{-1}$ — $8.5 \cdot 10^{-3}$ mol/l) and their *para*-substituted analogues in CHCl_3 (concentration $2.1 \cdot 10^{-5}$ mol/l) in a NaCl measuring cell having the sample path length of 0.5 mm. The choice of solvents and concentrations was limited by the poor solubility of the studied compounds. Deuteration of *ortho*-substituted phenols and of 1-(2-benzotriazolyl)-2-naphthol was achieved by shaking the tetrachloromethane with equal amount of heavy water for 10 min.

RESULTS AND DISCUSSION

The wavenumbers of the hydroxyl group stretching vibration in *para*-substituted phenols are summarized in Table I. Since these compounds cannot form an intramolecular hydrogen bond, the corresponding wavenumbers have values close to 3600 cm^{-1} and with increasing value of the Hammett's $\bar{\sigma}_p$ constant they are shifted towards the lower values. Derivatives containing the 2-[4,5]areneazolyl- or the 2-indolyl-substituent conform with the series of *para*-monosubstituted phenols giving an expected linear correlation between $\tilde{\nu}_{(\text{OH})}[\text{CHCl}_3]$ and $\bar{\sigma}_p$. The final equation obtained by least squares procedure has the form

$$\tilde{\nu}_{(\text{OH})} = 3600 - 17.2\bar{\sigma}_p, \quad s \ 3.94, \quad r \ 0.964, \quad n \ 12,$$

TABLE II

Wavenumbers of Bands Due to the OH and OD Stretching Vibrations of Some *ortho*-Substituted Phenols in CCl_4

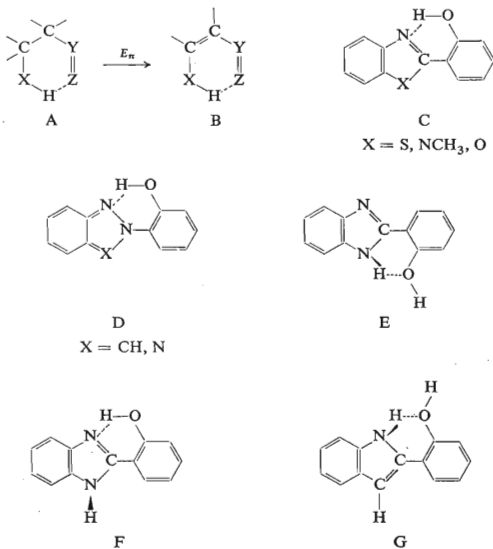
No	Substituent	$\tilde{\nu}_{(\text{OH})}$ cm^{-1}	$\tilde{\nu}_{(\text{OD})}$ cm^{-1}	$\frac{\tilde{\nu}_{(\text{OH})}}{\tilde{\nu}_{(\text{OD})}}$
XVII	2-benzthiazolyl	3 015 ^a	2 265	—
XVIII	acetyl	3 060 ^a	2 305	—
XIX	2-indazolyl	3 070 ^a	2 318	—
XX	N-methyl-2-benzimidazolyl	3 080 ^a	2 320	—
XXI	benzoyl	3 100	2 340	1.33
XXII	2-benzoxazolyl	3 154	2 376	1.33
XXIII	2-benzotriazolyl	3 171	2 399	1.33
XXIV	formyl	3 189	2 394	1.33
XXV	2-naphtho[1,2- <i>d</i>]triazolyl	3 206	2 413	1.33
XXVI	nitro	3 248	2 447	1.33
XXVII	2-benzimidazolyl ^b	—	—	—
XXVIII	2-indolyl ^c	3 611	2 671	1.35
XXIX	1-(2-benzotriazolyl)-2-naphthol ^d	3 266	2 430	1.34

^a Calculated from the measured values of $\tilde{\nu}_{(\text{OD})}$ using the relation $\tilde{\nu}_{(\text{OH})}/\tilde{\nu}_{(\text{OD})} = 1.33$. ^b Too low solubility, $\tilde{\nu}_{(\text{NH})}$ 3484 cm^{-1} , $\tilde{\nu}_{(\text{ND})}$ 2600 cm^{-1} , $\tilde{\nu}_{(\text{NH})}/\tilde{\nu}_{(\text{ND})} = 1.34$. ^c $\tilde{\nu}_{(\text{NH})}$ 3469 cm^{-1} , $\tilde{\nu}_{(\text{ND})}$ 2596 cm^{-1} , $\tilde{\nu}_{(\text{NH})}/\tilde{\nu}_{(\text{ND})} = 1.34$. ^d This compound has not the general structure given above.

where s is the standard error, r the correlation coefficient, and n the number of compounds in the calculated series.

Cohen and Jones¹⁸ found the value $\rho = -16.5$ for a similar dependence in 4-substituted 2,6-di-tert-butyl-phenols (CCl_4 solution) and Ingraham and coworkers¹⁹ found the values $\rho = -12.6$ and $\rho = -14.4$ for *para*-substituted phenols lacking the steric shielding (in CCl_4 and C_2Cl_4 , respectively). The OH bond is weakened with increasing value of σ_p^- and the wavenumber of the $\tilde{\nu}_{(\text{OH})}$ stretching vibration is shifted towards the lower values. Since there is a linear correlation between the $\text{p}K'$ values and the σ_p^- constants¹⁶, a linear correlation between the $\text{p}K'$ values and the $\tilde{\nu}_{(\text{OH})}$ values also exists. Thus, the obtained results confirm the validity of the σ_p^- constants of the nitrogen-containing 2-yl substituents¹⁶.

Infrared spectra of *ortho*-substituted phenols (with the exception of XXVIII) indicate strong intramolecular hydrogen bonding in these compounds (Table II). The wavenumbers of the hydroxyl group stretchings are shifted to the region of 3266 to 3015 cm^{-1} . These bands have a very low intensity and their width is about 300 to 500 cm^{-1} . Since the aromatic C—H vibrations and so-called pseudo-maxima²⁰ also appear in this region, the accurate determination of the wavenumbers is very difficult. With the compounds XVII—XX it was made possible using the appropriate deuterio derivatives and employing the fact of the constant $\tilde{\nu}_{(\text{OH})}/\tilde{\nu}_{(\text{OD})}$ ratio.



Even in this case, the determination of the position of the band maximum is accompanied by a relatively large error (about $\pm 10 \text{ cm}^{-1}$). The spectrum of 2-(2-benzthiazolyl)phenol before and after deuteration is shown in the Fig. 1 for illustration purposes. As can be seen from the Table II, the ratio $\tilde{\nu}_{(\text{OH})}/\tilde{\nu}_{(\text{OD})}$ is constant and equal to 1.33 in the *ortho*-substituted phenols having a strong intramolecular hydrogen bond. Merrill²¹ had found the value 1.32–1.35 for the derivatives of 2,2'-dihydroxybenzophenone and Hrdlovič¹⁰ had found the value 1.31–1.36 for the derivatives of 2-hydroxybenzophenone. This value is slightly greater (1.34) in the naphthol derivative and exhibits the largest value (1.35) in the compound in which the intramolecular hydrogen bridge is completely absent. In the derivatives containing a N—H group (XXVII and XXVIII), the substitution of this hydrogen for deuterium also takes place during the deuteration; of course, this reaction is somewhat slower than the O-deuteration. The exchange of the nitrogen proton is nearly 100% after 30 min. This observation is different from that made for instance with pyrrole, where the exchange amounts about 1/3–1/2 of the total value²² after 30 min. This fact indicates that the nitrogen lone pair is more localized on the nitrogen atom in the studied compounds than in pyrrole. The ratio $\tilde{\nu}_{(\text{NH})}/\tilde{\nu}_{(\text{ND})}$ is also constant and roughly equal to the $\tilde{\nu}_{(\text{OH})}/\tilde{\nu}_{(\text{OD})}$ ratio.

The relative strength of the intramolecular hydrogen bond in *ortho*-substituted phenols can be estimated using the wavenumbers of the hydroxyl group stretching vibrations, since this bond is not perturbed in the non-polar CCl_4 and no intermolecular solvent-solute or solute-solute interactions are present at the studied concentrations. The strongest intramolecular hydrogen bond was found in XVII. According to Shigorin^{23,24}, the energy of the intramolecular hydrogen bond is expressed as a sum of three terms

$$E = E_d + E_a + E_\pi, \quad (1)$$

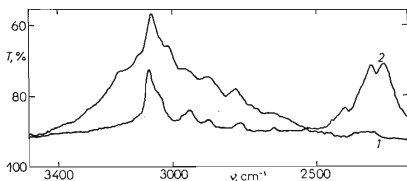


FIG. 1

IR Spectrum of 2-(2-Benzthiazolyl)phenol Before (curve 1) and After (curve 2) Deuteration with Deuterium Oxide

where E_d is the energy of the dipole interactions, E_a is the energy of the donor-acceptor interaction, and E_π is the energy of the π -electron interaction. The magnitudes of these terms are in order $E_\pi \gg E_a, E_d$. The term E_π means the energy change accompanying the transition from a cycle having unconjugated bonds (structure A) to a cycle having the conjugated bonds (structure B); the π -electrons of the X-atom also participate in the conjugation. All these requirements are met in the case of 2-(2-benzothiazolyl)phenol, since the π -electrons are strongly delocalized in this compound and its derivatives and all conditions for the formation of a new conjugated ring (structure C), containing an intramolecular hydrogen bond are fulfilled. The enhanced conjugation in the derivative XXVII is probably due to the presence of sulphur (which easily supplies its lone electron pair) in the heterocyclic ring so that the conjugation in the whole system of the structure C is enhanced¹⁶. In the compound XX (X=N—CH₃), the value of $\tilde{\nu}_{(\text{OH})}$ is shifted towards the higher values. The weakest intramolecular hydrogen bond from all the three mentioned compounds was found in the compound XXII (X=O). In the compounds having the structure C, the strength of the intramolecular hydrogen bond decreases with increasing electronegativity of the atom X. This order is completely reversed with respect to that of the relative stability of the intramolecular hydrogen bond in the same compounds found in 50% aqueous dioxane¹⁶. A similar situation exists in compounds of general structure D: the intramolecular hydrogen bond is stronger in XIX than in XXII whilst this order is reversed in protic solvents¹⁶. Generally speaking, the derivatives containing the triazolyl substituent exhibit the weakest intramolecular hydrogen bonds in the examined series of phenols *ortho*-substituted by a 2-(4,5-arene)azolyl radical (Table II). Since the 2-(2-indazolyl)phenol (XIX) and the derivatives having the triazolyl substituent exhibit also a relatively strong intramolecular hydrogen bond ($\tilde{\nu}_{(\text{OH})}$ 3270 cm⁻¹), it might be assumed that even in the structure B a new conjugated ring can be formed using an intramolecular hydrogen bond. The reason for the weakest hydrogen bond in the triazolyl derivatives is probably the lowest basicity of the nitrogen atoms of the triazolyl ring and also the lowest dipole moment (the lowest E_d and E_a) from all the studied compounds¹⁶.

Since some aromatic derivatives having an oxygen proton-accepting group were also measured (XVIII, XXI, XXIV, and XXV), it was possible to compare the bonds of the type N...H—O and O...H—O. From the results given in the Table II it is evident that no one from these types could be unambiguously considered as the stronger one. In the contrary, our results only support the theory of Shigorin^{23,24}, postulating the decisive role of the conjugation in the newly formed quasi-aromatic ring and the minor importance of the proton-donor and the dipole-dipole interactions, respectively.

The absolute strength of the intramolecular hydrogen bond (expressed as its energy) can be accurately determined from the temperature dependence of some physico-chemical property. However, this method is problematic even with the

compounds exhibiting strong intramolecular hydrogen bonding because of temperature independence of the studied property IR and NMR spectroscopies are so far the only methods assuring a reliable measurement at least of the relative strength of the intramolecular hydrogen bond. However, our preceding results^{16,17} indicate that the stability of this bond is strongly medium-dependent in the studied compounds, being most affected by protic solvents. The largest effect upon intramolecular hydrogen bonding was found in compounds having a basic proton-accepting group in the intramolecular hydrogen bond. Therefore it can be stated that the compounds having weakly proton-accepting groups (e.g. the compounds *XVIII*, *XXI*, *XXII*, and *XXIII*) exhibit a relatively strong hydrogen bond in the nonpolar solvents, since the presence of a strong intramolecular hydrogen bond (even if the relatively weakest one from the all studied *ortho*-substituted 2-[4,5]areneazoyl phenols) can be assumed also in the compound *XXIII* ($\tilde{\nu}_{(\text{OH})}$ 3171 cm^{-1}). Furthermore, the intramolecular hydrogen bond in these compounds has the largest stability towards the solvent effects¹⁶. The compounds *XVII*, *XIX*, and *XX* exhibit a strong intramolecular hydrogen bond in the non-polar media but this bond is relatively fast destroyed especially by the proton-donating solvents^{16,17}. A special note should be paid to the compounds *XXVII* and *XXVIII*. The 2-(2-benzimidazolyl)phenol has a very poor solubility in CCl_4 so that only the wavenumbers of the bands of the free N—H groups can be identified. However, from these values it follows that the simple bridge N—H...O (structure E) is improbable, since such a molecule should exhibit a remarkable shift of the $\tilde{\nu}_{(\text{NH})}$ towards the lower values and the $\tilde{\nu}_{(\text{OH})}$ should be near 3600 cm^{-1} or only slightly affected by the above mentioned type of the intramolecular hydrogen bonding. Therefore, the correct structure for *XVIII* should be written as F and not as E^{25,26}. In the 2-(2-indolyl)phenol neither an intramolecular hydrogen bond of the type O—H... π nor of the type N—H...O (structure G) are present. *ortho*- and *para*-Substituted phenols having a 2-indolyl group have therefore very similar values of the O—H group wavenumbers (Table I and II).

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